EFFECTS OF PHYSICAL STIMULII, AERATIGN, PRE-HEATING, ELECTRIC FIELD ON THE SUPER-COOLING AND NUCLEATION OF WATER DROPLETS

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ABSTRACT. Experimental results on the supercooling and nucleation of suspended droplets of sizes ranging from 1.7mm to 2.5mm as functions of low intensity shockwaves, electric field, aeration and preheating are presented. Natural freezing temperature ranged from −5.5°C to −6.5°C. With the superimposed conditions, in each case, the droplets took longer time to freeze and attained more supercooling. Shock waves of strength 1.1psi could not trigger freezing at warmer temperature as could be done in the case of bulk samples of water. An explanation for this discripancy has been put forward based on the physical structure and energy balance.

INTRODUCTOIN

The nucleation of ice in supercooled liquid water is a subject of great interest and importance not only to the field of cloud physics but also to other sciences since observations on supercooled water furnish useful information applicable to the nucleation mechanisms in the supercooled melts of other substances. Reviews of the investigations on nucleation reported in literature have been given by Dorsey (1948), Buckley (1951), Dunning (1955) Mason (1957), Van Hook (1961), Fletcher (1962), Kapustin (1963), Shubnikov *et al* (1963), Chalmers (1964) and Goyel *et al* (1965).

Bulk water freezes near 0°*C*, but water droplets remain liquid at much lower temperatures. Laboratory experiments have shown that the freezing temperatures of pure water droplets range from about −35°*C* for larger droplets to −41°C for the smallest. In nature, however, some cloud droplets, freeze at temperatures of −15°C or even warmer. The freezing temperature varies with composition, quantity, and size of the freezing nuclei present. Lonsdale (1958) has shown that the amount of ice-like structure present at 0°C varies from 32% to 70%. Davis and Litovitz (1965) estimated the structure of water to be approximately 60%

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ice-like at 0°C and 30% ice-like at 100°C. When such ice-like structures agglomerate to a certain critical size they may act as nuclei. The nucleation of a supercooled liquid by foreign crystals is highly specific, ice nucleates water at a tmperature very close to 0°C but no other substance is known which causes nucleation at a temperature higher than −5°C. Silver iodide, which is pseudo-morphic with ice is effective for temperatures below about −7°C. Friction or mechanical action in various forms, provides the only means at present known (othr than seeding by ice). Young and Van Sicklen (1913), found that water could be induced to freeze by very violent impacts of a hard steel point on a steel surface at temperatures above −0.1°C. Recently Bhadra (1968) has carried a series of experiments on dynamic nucleation of bulk samples of super-cooled water. He has been able to induce nucleation by the dynamics of the airbubbles liberated from the bulk samples by different physical methods, at temperatures above −5°C. In the absence of the dynamics of air bubbles, nucleation could not be produced at temperatures above −5°C. Since the structure of water is about 60% ice-like at 0°C, it is reasonable to suggest that dynamics of air bubbles would help the molecules to be maneuvered into the final correct position on the growing lattice in the bulk samples of supercooled water and the foreign nuclei if present play an insignificant role in this temperature range (0 to −5°C). Sensitivity of the foreign nuclei as nucleating agents is dependent on the structure as well as hygroscopic and thermal properties. In the lower range of supercooling of bulk water (0 to −5°C), ice nuclei appears to be the predominent nucleating agents on which the supercooled molecules are jockeyed when some kind of dynamics are developed in the system.

The freezing temperatures of droplets extend over wide range depending on size and environment. Literature on the freezing of water droplets is extensive; still the mechanisms involved in the process of nucleation are not clearly understood. This paper presents the results of experiments performed under various conditions on the freezing of supercooled water droplets. The principal object of the experiments described below was to determine whether physical stimulii induce freezing of supercooled wter droplets in the lower range of supercooling 0°C to 5°C as obtained in the case of bluk sample (Bhadra) and to study the effects of pre-heating and aeration of the samples supercooling and nucleation.

THEORETICAL

The formation of crystal embryos in supercooled samples is essentially a temperature activated rate process. While forming a crystal by chance aggregation of molecules, the free energy of the system passess through a maximum. The condition for equilibrium of the crystal embryos with the supercooled liquid is represented by $\psi_\beta - \psi_\alpha = \frac{2\gamma v_\alpha}{r} + p(v_\alpha - v_\beta)$ where ψ_β and ψ_α are respectively the molecular Helmholtz free energies of water and ice, v_β and v_α are respective molecular volume, r is the radius of the embryo, γ is the interfacial free energy and p is the pressure in the liquid. Embryo is taken here to be sperical.

No satisfactory kinetic calculation has yet been given for the crystallisation process on the basis of any model. Frenkel (1932) has given a theory based on the quasi-thermodynamic treatment of vapour condensation due to Volmer and Weber (1926). It may be argued on the basis of Einstein's fluctuation theory (1910) as Volmer and Weber did for droplet formation that the probability per cm^3 per sec that an embryo will form is given by

$$J = C \exp. (\Delta F_0/kT) \quad .. \quad (2)$$

where ΔF_0 is the work of formation of the embryo of equilibrium size, k is the Boltzman constant, T is the absolute temperature and C is a constant. Frenkel introducing the effect of viscous resistance to the free supply of molecules at the surface of embryo, modified the equation (2). His theory is summarised by the equation

$$J = C' \exp (-U+4\pi r^2\gamma/3)(1/kT) \quad .. \quad (3)$$

where U is the activation energy for viscous flow, and $4\pi r^2\gamma/3$ and $C' \exp(-U/kT)$ stand respectively for ΔF_0 and the constant C in equation (2).

The interfacial energy γ is beyond the existing experimental techniques to measure. Following Volmer's (1939) suggestion a value of 10.5 $ergs/cm^2$ is obtained for γ.

Since the first term of the equation (3), $e^{U/KT}$ decreases with lowering temperature, while the second term $e^{4\pi r^2\gamma/3KT}$ behaves conversely, the rate curves for both nucleation and growth will pass through maxima. The sharpness of transition stage will depend upon the parameters involved in each case. This pattern is shown in figure 1. Turnbull and Fisher (1949) obtained a value of roughly 10^{36} for C. According to Frank (1949), it is not obvious that an ice crystal should nucleate supercooled water easily in reality if the crystal were perfect, it almost certainly would not. Crystal surface imperfection plays an important role in the

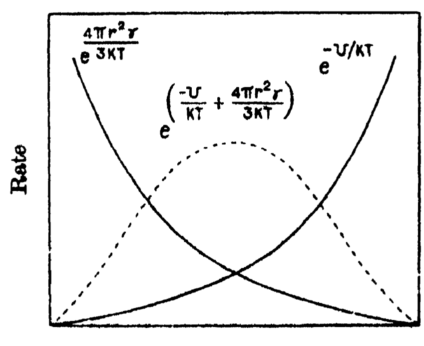

Figure 1. Composition of growth curve

process of crystallisation. It is expected that when a foreign crystal is introduced into a supercooled liquid and causes nucleation, its surface imperfections play an analogous role.

EXPERIMENTS

The natural freezing temperature is defined here as the temperature at which the sample freezes by slow cooling. Distilled water was used to make the droplets. The influence of any foreign particles present was taken into account in the natural freezing temperature. Any deviation from the natural freezing temperature of the samples, has been attributed to be due to the added factors such as shock waves, electric field, aeration and pre-heating.

Experimental procedures followed in these investigations are summarised in table 1.

Experiments were performed to study the effects of low intensity shock wave, electric field, contact with metal, aeration and preheating on supercooling and nucleation of water droplets having the dimensions ranging from 1.7 to 2.5 mm in diameters.

Droplets were formed (i) at the end of a capillary tygon tubing fitted to a syringe which served as a reservoir and (ii) on a steel plate. Samples were supercooled in a shock tube at a temperature of $-9°C$ to $-10°C$. The interior temperatures of the droplets were measured by means of micro-thermocouple. The tip of a micro-thermocouple probe was inserted into the droplet without appreciably deforming it. The output of the thermocouple after amplification by an electrometer (GE-1230A) was recorded by an $X-Y$ recorder. Phase change was detected by (i) the sharp rise of temperature and (ii) the shadowgraph technique (Goyer *et al* 1965).

Experiments (Nos. 1 and 2).

Droplets of sizes ranging from 1.8 to 2.5 mm. in diameter i) suspended from the tip of the tygon tubing and ii) placed on steel plate were subjected to shock over pressure of 1.1 p.s.i. when the droplets were supercooled to $-3°C$ to $-4°C$.

Experiments (No. 3)

Droplets of Sizes ranging from 1.7 to 1.9 mm. in diameter suspended from the tip of the tygon tubing were placed between two insulated metal plates acting as electrodes. D.C. electric field of 1.6KV/cm was applied between the plates. The droplets were allowed to cool under the influence of electric fields.

Experiments (No. 4)

Bulk samples of distilled water were aerated by the passage of air current through it. This aerated distilled water was taken into the syringe and droplets of size 1.9 mm. were formed out of it. Nucleation was produced by slow cooling process.

Table 1. Summarised experimental procedures

Water droplets

	Drop dimension	Temp. of the Shock tube	Initial conditions of the droplet sample	Process of nucleation
1. Shock tube	(1.7 to 2.5)mm in diameter	-9° to $-10^{\circ}C$	$-3^{\circ}C$ to $-4^{\circ}C$ suspended at the end of a tygon tubing.	Shock wave
2. ,,	,,	,,	-3° to $-4^{\circ}C$ placed on a steel plate	Stimulated by shock wave.
3. ,,	,,	,,	Aerated sample suspen- at the end of a tygon tubing.	Normal cooling.
4. ,,	,,	,,	pre-heated sample sus-pended at the end of a tygon tubing.	Normal cooling.
5. ,,	,,	,,	Droplet suspended bet-ween two insulated metal plates acting as electrodes	1.6 KV D.C. Electric field

Experiments (No. 5)

Bulk samples of distilled water were preheated near boiling point for about 15 minutes. The preheated water was taken into the syringe and droplets of the size 1.7 mm were formed out of it. Nucleation was produced by slow cooling process.

Each of these experiments was repeated at least five times.

The freezing temperature and the time required to freeze the droplets were recorded simultaneously. The recordings were initiated at the time the droplet was formed inside the shock-tube by pushing the piston of the syringe.

RESULTS

The natural freezing temperature of the droplets varied between −5.5°C to −6.5°C when the environmental temperature inside the shock tube was −9°C to −10°C. Figures 2(a) and 2(b) show the shadowgraph pictures of the droplet in the liquid state and solid state respectively.

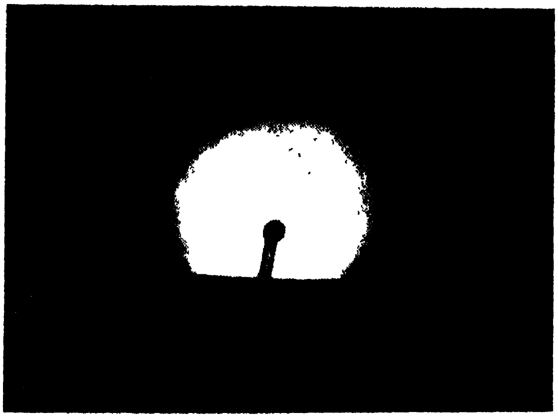

Figure 2 (a)

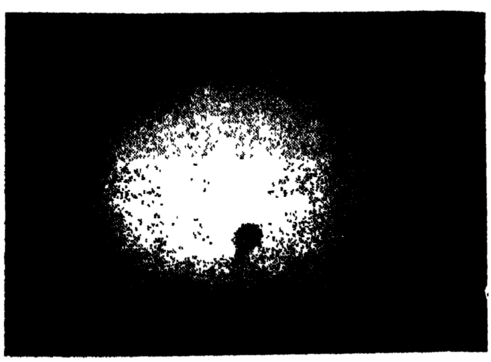

Figure 2 (b)

Results are summarised in table 2. The result shown in each row is the average of at least five observations. The maximum probable errors are $\pm 0.5°C$ and ± 1 sec.

Table 2

Freezing of supercooled distilled water droplets.

				Average freezing Temperature —				
Sl. No.	I Drop size in mm.	II Chamber Tempera-ture $-°C$	III Freezing time in min.	IV Natural	V Shock wave 1.1 psi.	VI Electric field 1.6KV/cm	VII Aeration	VIII Water Pre-heated for 15 min.
1	2.5	9.2	9.8	6.5				
2	2.5	9.2	**18.1**		7.5			
3	1 8	9.8	7.4	5.5				
4	2.0	9.8	**18.9**		8.0			
5	1 8	9.8	**25.7**		8.0			
6	1.8	9.8	9.3	6.0				
7	1.8	9.8	**14.9**		7.5			
8	1.9	9.0	6.1	5.5				
9	2.1	9.0	6.5	6.0				
10	1 7	9.0	**9.3**			6.8		
11	1.9	9.0	**21.5**			6.9		
			Observed for					
12	1.9	9.5	**27min**				6.8 (not frozen)	
13	1.9	9.5	**30min**				7.0 (not frozen)	
14	1.7	9.5	**36.4 min**					8.0 (not frozen)
15	1.7	9.5	**40 min**					8.0 (not frozen)

*Results in each row represent the average of at least 5 observations.

(1) Low intensity shock waves (1.1 psi) applied at ($-3°C$ to $-4°C$), could not trigger freezing of the supercooled droplet but produced tremoring which was observed in the shadowgraph. In some cases, the droplets were blown awayfr om the tip of the capillary tube by the incident shock wave. Trajectories of these droplets could not be traced out. Occasionally fragments of the droplets shattered by the impact of the shock pressure larger than 1.1 psi got stuck to some parts

of the suspending system and froze. On critical examination of the frozen droplets erruptic structures on the surface of some of the droplets were found. Further it was observed that the entire body of the frozen droplets did not appear uniformly transparent and some part appeared foggy. Freezing was delayed due to the interaction with shock waves and more supercooling was attained.

(2) Droplets placed on a stainless steel plate froze naturally at $-6.0° \pm 0.5°C$. Low intensity shock waves applied at ($-3°C$ to $-4°C$) failed to trigger freezing of the droplets placed in contact with steel plate. Freezing was delayed, when the droplets were exposed to shock waves and more supercooling was attained.

(3) Droplets subjected to D.C. electric field of 1.6 KV/cm could not induce nucleation at warmer temperature. Uder the influence of this electric field the droplets attained more supercooling.

(4) Droplets formed from water saturated with air and

(5) droplets formed from pre-heated water, attained more super-cooling and took longer time.

In each case, the droplets were more supercooled and took longer time to freeze due to the additional conditions imposed on the droplets.

DISCUSSIONS

The equilibrium condition of a free droplet can be represented in a simplified form by the following equation

$$p_v = p_0 + \frac{2\sigma}{r} \qquad .. \quad (4)$$

where p_v the pressure due to the fluid forming the droplet, p_0—the ambient pressure, σ—the surface tension and r—the radius of the droplet. In the present investigations the droplet is not free. It is suspended from the tip of a tygon capillary tubing or placed on a steel plate. For the sake of simplicity it will be considered that the droplet is spherical. Free droplets prevail in the atmosphere.

It is clear from this equation that the force due to surface tension $2\sigma/r$ and the ambient pressure p_0 act on the droplet to squeeze it but the pressure due to the fluid composing the droplet opposes these two forces. The pressure inside the droplet is larger than the ambient pressure by $2\sigma/r$.

The free energy of the droplet may be calculated by using the following formula.

$$F \text{ drop} = Vf_0 + A\sigma \qquad .. \quad (5)$$

where f_0 is the free energy per unit volume of the bulk liquid, V the volume, A the surface area and σ the surface tension. The free energy consists of two parts, one proportional to volume and other to area of surface. The equilibrium state of the system maintained at constant volume and temperature is that of minimum free energy and the tendency for a liquid drop to assume a spherical shape is a simple manifestation of this rule, since a sphere has the minimum surface area for a given volume. In the case of a droplet whose dimensions are much greater than the range of the molecular forces, the major contribution to the free energy is a term proportional to the volume and the molecular behaviour is affected by the surface close to it. It is most likely that a thin layer of solid ice crust is formed on the surface of the droplet when it is placed in a cooled atmosphere. This structure presents a temperature barrier for heat transport as well as a resistance to any to physical change.

When the droplet freezes, there will be associated changes of (i) volume, (ii) temperature, and (iii) pressure. Clausius-Clapeyron equation representing these changes is given by

$$\frac{dp}{dT} = \frac{L}{T(v_\alpha - v_\beta)} \tag{6}$$

where dp is the change of pressure, dT change of temperature, L latent heat of freezing, T the absolute temperature and v_α, v_β the volumes of the liquid phase and the solid phase respectively. This equation states that a change of transition pressure dp equal to $L/T\Delta V$. dT results upon a change of temperature dT. A change of temperature of 0.0075° corresponds to a pressure change of 1 atmosphere. The water droplet increases in volume on freezing. The force due to surface tension and the ambient pressure oppose the volume expansion. In order that volume be increased, the pressure inside the droplet must exceed the opposing pressures. The pressure inside the droplet increases due to the pressure of crystallisation. The force due to surface tension, when the radius is 0.1 cm turns out to be of the order of 1480 dynes, assuming $\sigma = 74$ dyn/cm and $p_0 = 10^6$ dynes. This estimate indicates the magnitude of p at equilibrium condition. In the present investigations it has been observed in most cases, that erruptic rupture on the surface of the droplet occurred at the time of freezing. This indicates the formation of a thin layer of solid crust on the surface. In other cases, the shadowgraphs showed deviation from circular cross-section on freezing. This indicates that till that time no solid crust was formed. So long the volume increase is restricted, water in the droplet remains in the liquid state and attains more supercooling. In order that the volume be increased, the magnitude of pressure of crystallisation must exceed by 1480 dynes in the case of droplet of radius 0.1 cm.

Further, the pressure is proportional to the thermal energy per unit volume and varies in the following way.

$$p = p_0(R_0/R)^{3\Gamma} \tag{7}$$

Where p_0 and R_0 are the initial pressure and radius respectively and Γ is a parameter which takes account of the fact that the expansion of heated zone may be accompanied by the expenditure of thermal energy in doing work.

The supercooled droplets on phase transition is heated up by the thermal energy released by latent heat of crystallisation.

Equations (4), (5), (6) and (7) elucidate the physical principles involved in the process of nucleation of supercooled liquid droplets. Attempts are made to interpret the results of the present investigations in terms of these principles.

Goyer *et al* (1965) and Bhadra (1968) have demonstrated that low intensity shock wave and physical stimulii can trigger nucleation in bulk samples of supercooled water. Small samples of water contained in glass tube were triggered to nucleate by the impact of 1.1 psi shock wave. The impact of the shock waves released the air bubbles trapped in water and at the interface between water and the wall of the container. Air bubbles while moving to the surface grew in size and ultimately escaped into the atmosphere. The growth and movement of the air bubbles created a dynamic system in the liquid sample. Induced nucleation occurred in bulk sample of supercooled water, when there air bubbles generated inside the sample. In the absence of air bubbles induced nucleation was not observed. The mechanism of nucleation has been termed by the author as dynamic nucleation. It has been pointed in the beginning of the dicussion that the movements of the atoms constituting the liquid are essential for crystallisation.

But in the case of suspended droplets, low intensity shock wave of strength 1.1 psi could not induce freezing at warmer temperature. In all cases the freezing was delayed and more supercooling was attained. The droplet as a whole was put into jerking motion due to the impact of shock wave but still the droplet did not freeze.

As a plausible explanation it may be suggested here that because of unbalanced pressure developed on the droplet due to the impact of the shock waves, atoms gained acceleration with the consequent rise of temperature of the droplet and the melting of the embryonic crystals, which might be attributed to be causes of delay in freezing and of attainment of higher degree of superzooling. These observations are in agreement with those obtained by Lowitz in bulk water. The droplets placed in contact with a stainless steel plate produced the same results as observed in the case of suspended droplt. Stainless steel plate did not add any noticeable influence on the freezing temperature.

In these cases air bubbles might have been produced by the shock waves in droplets, but they could not grow or produce the requisite dynamics in the systems because of the lack of a proper pressure gradient and of the space required for the appropriate growth. The droplet sizes varied from 1.7 mm to 2.5 mm and within this thickness of the medium, shock waves could not produce any pressure gradient i.e., the pressure all round the droplets was practically constant.

It has been observed that the fragments of the droplets shattered by the impact of shock waves, froze almost instantaneously. Balanchard (1950) has demonstrated the shattering of droplets in a wind tunnel and Hanson *et al* (1963) in a shock tube. In the present investigations droplets were not free. The energy transferred to the droplet by the impact of the shock wave, was expended in shattering the droplets. In the case of the free droplets as found in the atmosphere, the energy transferred to the droplet by the impact of the shock wave, would be expended in the motion of translation, thereby increasing the probability of the number of collisions among the droplets and as a result coalescence of the droplets also would increase. The dynamics generated by the coalescence of the droplets may also initiate the freezing of the supercooled droplets.

Further, the zone behind the shock front is the high temperature zone. When the supercooled droplets enter into the high temperature zone, the kinetic energy of the droplets increases so evaporation takes place from the surface of the droplets Depending upon the size of the droplets and the temperature of the zone, some will be completely evaporated and some will attain more supercooling due to the evaporation from the surface and ultimately initiate freezing due to the existing fluctuation.

These arguments indicate the plausibility of using shock waves in various forms to modify the atmospheric supercooled cloud droplets.

It is well known (Lowitz, 1795 and Dorsey, 1948) that the degree of supercooling attained in a droplet depends considerably upon the history and previous treatment of the samples. Previous heating of the samples or removal of the first crystals formed increases the supercooling.

In the present investigations, droplets formed out of preheated and aerated water, could be supercooled to lower temperature than the normal freezing temperature ranging from $-5.5°C$ to $-6.5°C$. These results indicate a modification of the local structure.

1.6 KV/cm D.C. electric field produced higher supercooling on droplets. Water molecules are polar. Under the influence of the field, it is likely that orientation of the dipole in the direction favourable for crystal growth might be hindered causing thereby the delayed freezing and higher supercooling. Mason (1957) and Pruppacher (1963) have discussed the effects of electric field on crystallization.

From the results shown in table 2, it is clear that in all cases, the droplets took longer time to freeze and attained higher degree of supercolling. The fundamental mechanism remaining the same, the effectiveness of the added conditions on the samples, manifest differently in the cases of bulk, suspended droplet and free droplet. While studying the problem of nucleation, it is not the time factor but the freezing temperature is the important parameter to be determined experimentally. In the present investigations, it is apparent from the table 2 that longer the time to freeze, the greater is the degree of supercolling. It has been experimentally determined that samples of the same size take the same length of time to freeze provided the environmental conditions remain the same.

Further investigations on droplets under varied conditions are in progress.

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